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Alternative fuels: An overview of current trends and scope for future

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ABSTRACT

The concern over rapid depletion of fossil fuels has prompted the search for alternative fuels having efficiencies similar to those found for the conventional fuels being used today. The present article reviews the prospects and opportunities for using alternative fuels in different applications. The properties of these fuels and their performance as a fuel are discussed in detail. Vegetable oils present a very promising scenario of functioning as alternatives to fossil fuels. Use of biodiesel in a conventional diesel engine results in a substantial reduction in unburned hydrocarbons, carbon monoxide, particulate matter, and nitrogen oxides. Different alternative fuels have been compared with the conventional fuels, and clearly the consumption of the latter can be significantly decreased by the use the blended fuels.

Most of the alternative fuels have properties similar to those of the existing fuels, and therefore the technology required to handle them is already well known. Hydrogen is an exception to this, and its ignition properties are quite different from those of the conventional fuels. Difficulties are thus expected during the storage, transport, and use of hydrogen as a fuel. Other technologies are also discussed such as alternative routes to equivalents of conventional fuels, like CTL. Finally, the emulsified fuels including the use of oxygenates have been discussed.

Contents

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1. Introduction

The fossil fuels present on our planet are limited. The conventional fuels are also a net source of green house gases. Before we run out of fossil fuels, we will have to look for other alternatives for fuels and for sources of energy. A lot of efforts are currently going on worldwide to find alternative fuels which may meet our present and future demands of energy, without causing further global-warming effects.

A comparative study of literature on various alternative fuels such as ethanol, vegetable oils, glycerol, biomass, biodiesel, diethyl ether, hydrogen, etc., and their impact on the environment has been attempted here. The article presents an extensive review of the raw materials' properties, details of manufacture and processing steps with a critical assessment of the viability of these different alternative fuels. For a fuel to be effectively used as an alternative to the conventional fuels, it should be comparable to the conventional fuels with respect to certain important properties such as ignition properties and combustion properties, which characterize the use of a material as a fuel. These properties are first defined in the following section.

2. Ignition and combustion properties of a fuel

2.1. Cetane number

Cetane number is defined as the volume of n-cetane in a mixture of n-cetane and α-methyl naphthalene, which gives the same ignition delay as the fuel under consideration, when tested in a Cooperative Fuel Research (CFR) engine. Ignition delay is the delay between the start of injection and start of combustion of the fuel. It represents the ignition quality of diesel fuel. Fuels with a higher cetane number will have a lower ignition delay period than the fuels with a lower cetane number. The cetane number is generally specific to a particular engine being used [1].

2.2. Calorific value

The heat of combustion is a direct measure of the energy content of a fuel. It is determined in terms of the quantity of heat liberated by the combustion of a unit quantity of fuel with oxygen in a standard bomb calorimeter. There are two heats of combustion, or calorific values, for every petroleum fuel, gross and net. When hydrocarbons are burnt, one of the products of combustion is water vapor. The gross calorific value includes the heat given off by the water vapor in condensing whereas the net value does not include this heat [1].

2.3. Octane number

Combustion in the spark ignition engine depends chiefly on engine design and gasoline quality. Under ideal conditions, the flame initiated at the sparking plug spreads evenly across the combustion space until all the gasoline has been burnt. The increase in temperature caused by the spreading of the flame results in an increase in pressure in the end gas zone, which is that part of the gasoline–air mixture where the flame has not yet reached. The increase in temperature and pressure in the end gas zone causes the gasoline to undergo pre-flame reactions. Among the main pre-flame reaction products are the highly temperature-sensitive peroxides. If these exceed a certain critical threshold concentration, the end gas will spontaneously ignite even before the arrival of the flame front emanating from the sparking plug, thus causing detonation or knocking. On the other hand, if the flame front reaches the end gas zone before the buildup of the critical threshold peroxides' concentration, the combustion of the gasoline–air mixture will be without knock. The various types of hydrocarbons in gasoline behave differently in their pre-flame reactions, and hence the differences in their tendency to knock. The octane number of a fuel is a measure of the knock rating of a gasoline, and is expressed as the percentage by volume of iso-octane (octane number 100, by definition) in a mixture of iso-octane and normal heptane (octane number 0, by definition), that has the same knock characteristics as the gasoline being assessed. Normal heptane and normal pentane, both paraffins, have anti-knock ratings (octane numbers) of 0 and 61.9, respectively [2].

2.4. Flash point

This is defined as the minimum temperature at which the vapors from an oil sample will give a momentary flash on application of a standard flame under specific test conditions. Abel flash point apparatus, Pensky–Martens closed cup apparatus and Cleveland open cup apparatus are the test apparatuses frequently used for the measurement of the flash point. Flash point is a parameter that can predict the possible fire hazards during transportation, handling, and storage of a fuel [1].

2.5. Volatility

The volatility of a liquid is its tendency to change from the liquid to the vapor or gaseous state. It is a primary and necessary characteristic of most liquid gasoline fuels. The distillation profile is also a measure of the relative amounts of the gasoline constituents in petroleum. The volatility of gasoline affects the performance of the engine in a number of ways, the chief ones of which are ease of starting, rate of warm-up, vapor lock, carburetor icing, and crankcase dilution (the dilution of the engine lubricating oil with the higher-boiling constituents of the gasoline).

Table 1
Characteristics of some pure vegetable oils [4].

Pure vegetable oil	Iodine value	CN	Low heat value (kJ/kg)	Viscosity (mm^2/s(C))	CP	PP (°C)	FP (°C)	Density (kg/L)	Sulfur (%)	Carbon residue (%)	Ash (%)
Neem seeds	–	47.0	39,399	30.0 (30°)	–	–	180	–	0.01	–	–
Karanja	–		37,100	120 (20°)	–	–	–	–	0.01	–	–
Mahua	–	45.0	30,248	16.9 (30°)	–	–	99	–	0.01	–	–
Jatropha	–	42.5	39,774	49.9 (38°)	–	–	–	–	0.01	–	–
Cotton seed	90–140	41.8	39,468	33.5 (38°)	1.7	−15.0	234	0.91	0.01	0.24	0.010
Sunflower	110–143	37.1	39,575	37.1 (38°)	7.2	−15.0	274	0.92	0.01	0.23	0.010
Soybean	117–143	37.9	39,623	32.6 (38°)	−3.9	−12.2	254	0.91	0.01	0.27	0.010
Sesame	104–120	40.2	39,349	35.5 (38°)	−3.9	−9.4	260	0.91	0.01	0.25	0.010
Safflower	126–152	41.3	39,519	31.3 (38°)	18.3	−6.7	260	0.91	0.01	0.25	0.006
Coconut	6–12	–	–	–	–	–	–	–	0.01	–	–
Olive	75–94	–	–	–	–	–	–	–	0.01	–	–
Palm	35–61	42.0	36,553	39.6 (38°)	31.0	–	267	0.92	0.01	–	–
Peanut	80–106	41.8	39,782	39.6 (38°)	12.8	−6.7	271	0.90	0.01	0.24	0.005
Corn	103–140	37.6	39,500	34.9 (38°)	−1.1	−40.0	277	0.91	0.01	0.24	0.010
Castor	82–88		39,500	297 (38°)	–	−31.7	260	–	0.01	–	–
Crambe	93	44.6	40,482	53.6 (38°)	10.0	−12.2	274	0.90	0.01	0.23	0.050
Rapeseed	94–120	37.6	39,709	37.0 (38°)	−3.9	−31.7	246	0.91	0.01	0.30	0.054
Linseed	168–204	34.6	39,307	27.2 (38°)	1.7	−15.0	241	0.92	0.01	0.22	0.010
Average bunker HFO	–	–	40,000–41,000	180.0–380 (50 °C)	–	−6, …,+6	60	0.96–0.99	2–3.5	8–16	0.03–0.07

CN—cetane number, CP—cloud point, PP—pour point and FP—flash point.

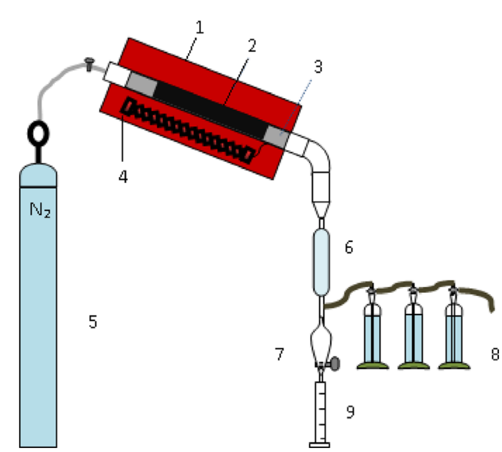


Fig. 1. Laboratory-scale batch mode equipment of LTC process. 1—oven; 2—dried sample; 3—glass wool; 4—electric resistance; 5—gas (N_2) cylinder; 6—condenser; 7 and 9—separator funnel; 8—gas washing bubblers [7].

The gasoline must be sufficiently volatile to give easy starting, rapid warm up, and adequate vaporization for proper distribution between the cylinders. At the same time, it must not be so volatile that vapor losses from the gasoline tank are excessive or that vapor is formed in the gasoline line, causing vapor lock that may impede the flow of gasoline to the carburetor [1].

2.6. Auto ignition temperature

The auto ignition temperature is a property of the fuels in gaseous and vapor forms. It is defined as the temperature at which the vapor ignites spontaneously in a confined space. There are standard test methods, such as the one described in the International Electrotechnical Committee Standards (IEC Standard 60079-4, 1975), which usually use a small conical glass flask as the test apparatus together with some other accessories. As the ignition is driven by the exothermic heat of oxidation, the reaction progresses to ignition only if the heat losses are less than the heat produced [1]. Within a large space, the cooling is much lower than in a small flask, so the auto ignition temperature becomes lower. Thus, safety concerns can become serious at larger scales of storage of inflammable fuels.

3. Alternative fuels

Currently, a variety of substances and their natural sources are being investigated as potential alternatives for fossil fuels, especially petroleum-derived fuels. The criteria for use depend largely on how the substance compares with standard fossil fuels with respect to the various desired fuel characteristics/properties discussed in Section 2. Some of the most popular ones being investigated are various oils—either pure, or as admixtures in suitable proportions with conventional fuels, ethanol, glycerol, biodiesel, and hydrogen. Liquid fuels generated from coal via the Coal to Liquid (CTL) technology can also serve as a viable alternative to the conventional gasoline or diesel. These alternatives are discussed in some detail in the following sections.

3.1. Vegetable oils

Vegetable oils are lipids derived from the plants. Pure vegetable oils, as well as blends of these vegetable oils with conventional fuels, have attained importance as possible alternatives to the conventional fuels on account of the triglycerides-of-fatty-acids content present in these oils, which can give useful hydrocarbons upon thermal cracking [3]. A series of thermal-cracking reactions were carried out for different oils which resulted in production of alkanes, fatty acids, and esters. Table 1 gives the characteristics of some pure vegetable oils which can be considered for use as alternative fuels. Pure vegetable oils can substitute heavy oils, particularly in low speed diesel engines such as those of large ships, as these neither produce net carbon dioxide nor generate sulfur oxides during their full life time, due either to the absence of sulfur or very negligible amounts of sulfur present in them. A major disadvantage concerning their use is that these can cause an increase in NOx emissions. However, appropriate engine adjustments can minimize the NOx emissions to a large extent. All the current technical methods for storage and distribution are also compatible with the use of pure vegetable oils [4–11].

Pure vegetable oils, also called "straight vegetable oils" (SVOs), can be used directly in diesel engines, with minor modifications. Preheated crude sunflower oils at 75 °C give the same heat release curve and gas cylinder pressures as those of diesel in a direct injection engine. The emissions' studies of the oil show that there is a decrease in carbon emissions, and smoke opacity by 2.05% and 4%, respectively [9]. Blends of vegetable oils and diesel, in appropriate proportions, also serve as a useful alternative to the conventional fuels or pure vegetable oils. A blend of Putranjiva oil (oil obtained from seeds of Putranjiva roxburghii) with diesel has been used in Ricardo Variable Compression Diesel Engine and it is reported that a blend of 30% of Putranjiva oil and diesel gives the best performance, equivalent to that when pure diesel is used, with significantly reduced CO, NO_X, and smoke-particulate emissions. Hence, a better alternative to pure diesel is a blend of Putranjiva oil and diesel which will decrease not only the consumption rate of diesel, but also the pollutants' emissions into atmosphere [5].

On similar lines, Hebbal et al. reported that a blend of 25% Deccan Hemp oil with diesel without heating, and up to 50% blend with heating, can be used as a substitute for diesel without any engine modifications [6]. The maximum efficiency of the 50% blend is comparable with diesel, but it has a disadvantage of larger emissions than diesel. The smoke, unburnt hydrocarbons, and CO have approximate percentages of 51.74%, 71.4%, and 33.3%, respectively [6].

It was observed by Al-Hasan et al. that the addition of *Pistacia palaestina* oil to the diesel fuel and increasing the percentage of the oil in diesel decreased both the brake power and thermal efficiency of the test engine and increased the brake specific fuel consumption. It, however, helped in reducing the particulates' emissions. This oil can be easily produced from fruits by pressing without needing any expensive techniques [11].

Engler and group found that re-refined sun flower oil can be used in diesel engines with very encouraging results. It was found that the degummed and de-waxed vegetable oil prevented engine failure [9]. The modified sunflower oil was found to be more promising than raw sunflower oil in terms of a satisfactory performance as a fuel. There were, however, problems with the long-term use because the sunflower oil caused a lot of carbonization in the engine [9].

Pyrolysis oil can be obtained from castor-oil seeds using a low-temperature conversion (LTC) process. A laboratory scale set-up of a batch process is shown in Fig. 1. The castor seed sample is placed centrally in a cylindrical glass tube surrounded by a cylindrical oven capable of ramping up the temperature at a predetermined rate. The glass tube is connected to a condenser. Nitrogen gas is purged through the system and then continuously passed through the sample throughout the process. After 10 min of purging, heating is started at a rate of 10 °C/min until a temperature of 380 °C is reached. This temperature is maintained for 2 h. The pyrolysis oil, water fraction and condensable gases are collected into a separator and separated on the basis of density difference, whereas the uncondensed gas is passed successively through three traps containing solutions of 10% NaOH (w/v), 10% $NaHCO_3$ (w/v) and 10% HCl (w/v). The pyrolytic char is retained at the middle of the reactor and collected after cooling [1]. The LTC process used for the production of pyrolysis oil is simple and cheap, and gives the pyrolysis product with 50% (w/w) of pyrolysis oil. One of the major advantages of castor plants is that they can be cultivated even in adverse environmental conditions, such as extreme drought conditions. This pyrolysis oil can be used as a blend with diesel in diesel engines, and the then ongoing research of this group aimed at improving the characteristics of the blend [7].

A blend of diethyl ether (DEE) with orange oil has a higher brake efficiency, peak cylinder pressure, and heat release rate in comparison to diesel or blends of orange oil and diesel. The DEE and orange-oil blend has lower emissions of HCs, CO, and smoke, but leads to higher emissions of NOx [8]. There is a rising interest in investigation of the suitability of dimethyl ether as a promising fuel, because of its neatness and high calorific value [12].

Water-and-vegetable-oil emulsions are also being explored as it has been observed that addition of water to vegetable oils decreases the concentration of NOx and hydrocarbons. A higher concentration of CO in the exhaust however calls for more research in this area [13–17].

3.2. Bio-ethanol

Alcohol has been used as a fuel for auto-engines since the 19th century. It is, however, not widely used because of its high cost. Ethanol has a lower heating value (LHV) of 26.9 GJ/t, air–fuel ratio (A/F) of 9.0, oxygen content of 34.8% (by mass), latent heat of vaporization of 842 kJ kg^{-1}, Reid vapour pressure (RVP) of 22 kPa, and octane number of eight. In recent years, this fuel has been gaining in importance, specifically as a transport fuel when mixed with gasoline, due to a number of advantages it offers. The most significant advantage is that it can be produced from biomass, which gives it the "green" status. It uses a carbon source which is already in circulation in the global cycle and not locked up as in the case of fossil fuels. The use of bio-ethanol thus helps to maintain the global green house gas (GHG) balance. Besides this, the other advantages are it has a better anti-knock property than gasoline, and low emissions of CO and unburnt hydrocarbons, it is safe to store and transport because of its high flash point and auto ignition temperature, and its molecule contains one oxygen atom which makes it a partially oxidized hydrocarbon. It is produced by conventional fermentation, and distillation, of a variety of biomass such as molasses, corn, beet sugar, sugar, cellulosic and lignocellulosic biomass, using various enzymes (cellulase, hemicellulase, cellobiohydrolases, endoglucanase, α-L-arabinofuranosidase, α-glucuronidase, β-xylanase, β-xylosidase, β-mannanase, α-galactosidase) and micro-organisms (*Escherichia coli*, *Filamentous fungus*, *Pischia stipitis*, *Zymomonas mobilis*, *Saccharomyces cerevisiae*, *Clostridium phytofermentans*). The production of ethanol from the cellulosic and hemicellulosic biomass requires some pretreatment so that the sugars become available to the enzyme or microorganisms for fermentation. During the pretreatment and acid hydrolysis, acetic acid is produced from hemicelluloses. Processing of lignocellulosic biomass also produces substances such as furans, weak acids, and phenolic compounds. These serve

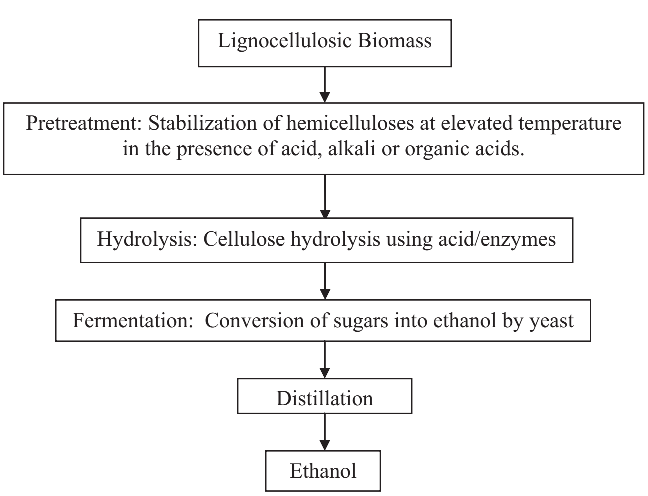


Fig. 2. Schematic representation of the process for conversion of lignocellulosic raw material to ethanol.

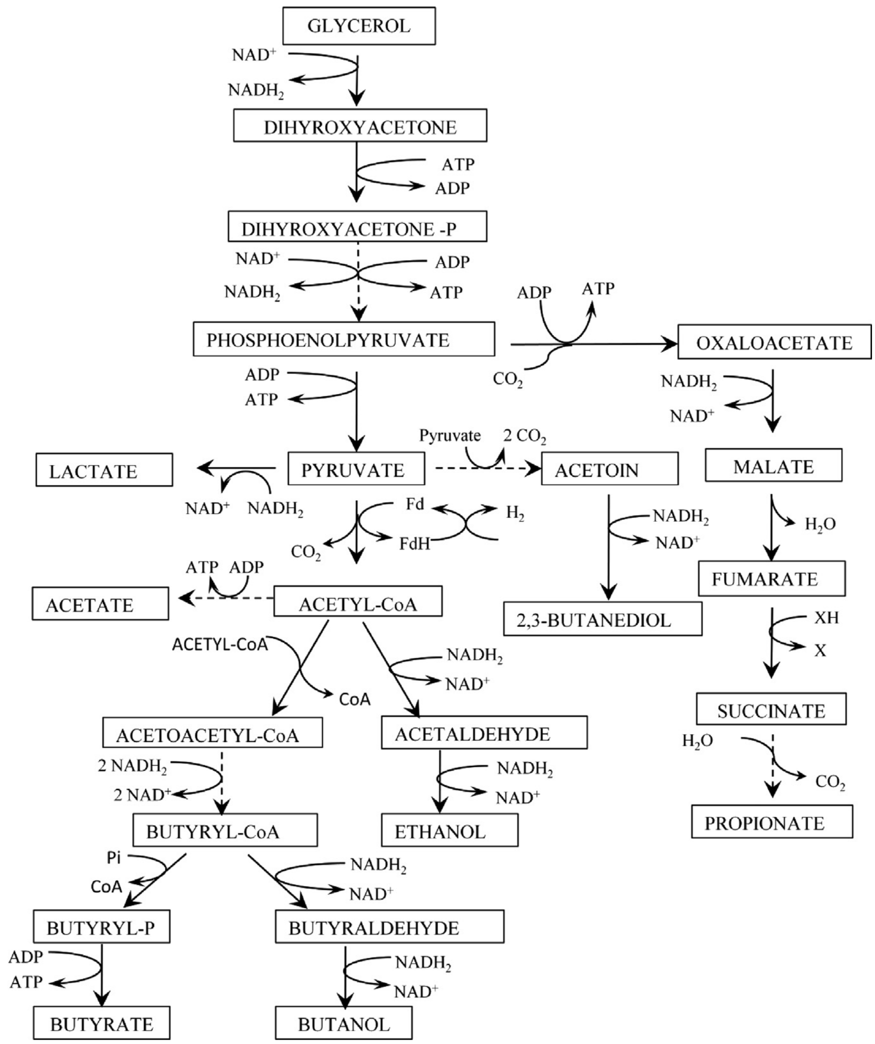


Fig. 3. Overview of some possible end products during glycerol degradation [26].

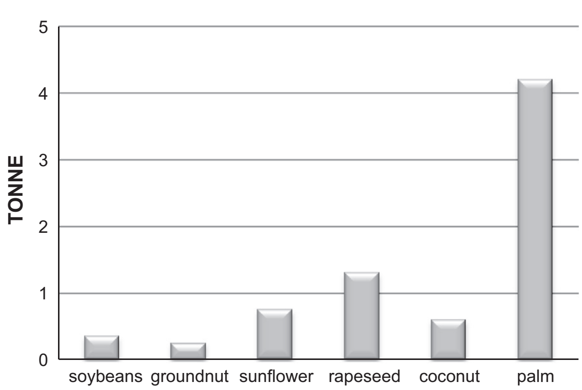


Fig. 4. Yields of selected vegetable oils (oil/ha/year, 2004–2006 average) [10].

as fermentation inhibitors which significantly affect the activity and life span of the micro-organisms, and reduce the yield of fermentation [18–20]. *S. cerevisae* is the most commonly used strain for ethanol production due to its well defined physiology and genetics. It produces a high yield of ethanol and is highly stress tolerant with a conversion efficiency of 90–95% of the theoretical value and final ethanol concentration of 10–16% (w/v) [21]. Fig. 2 gives an overview of the steps involved in the processing of lignocellulosic biomass for obtaining ethanol.

Ethanol, obtained from biomass in the fermentation processes outlined above, is in the form of an aqueous solution commonly called hydrous alcohol. This hydrous alcohol, if used as such and in common perception, may cause corrosion-related problems in the engine when used with gasoline as a transport fuel. Hence, the hydrous ethanol needs to be first concentrated, and further dehydrated in order to be used commercially as an oxygenate for gasoline [22].

In spite of all the advantages of using bio-ethanol as a transport fuel, there are certain limitations which also deserve a mention. An important limitation of ethanol as a transport fuel is that, being miscible with water, it may result into corrosion of the metallic engine parts. It can also react with rubber (but not with fluorocarbon rubbers). The latent heat of vaporization of ethanol is 3–5 times higher than of gasoline, hence the heating value of ethanol is lower. Therefore, more ethanol is required than gasoline for the generation of the same amount of energy. Blending of ethanol with gasoline can balance the advantages and limitations to give an optimum performance. Palmer reports that 10%-ethanol blending with gasoline increases the engine power output by 5% [23]. The octane number is enhanced by 5% for each 10%-blended ethanol. The effect of 10%-, 20%-, 30%-, and 40%-ethanol blended fuels in a variable-compression-ratio engine has been tested by Abdel-Rahman and Osman [24]. They report that an increase in the amount of ethanol results in a decrease in the heating value,

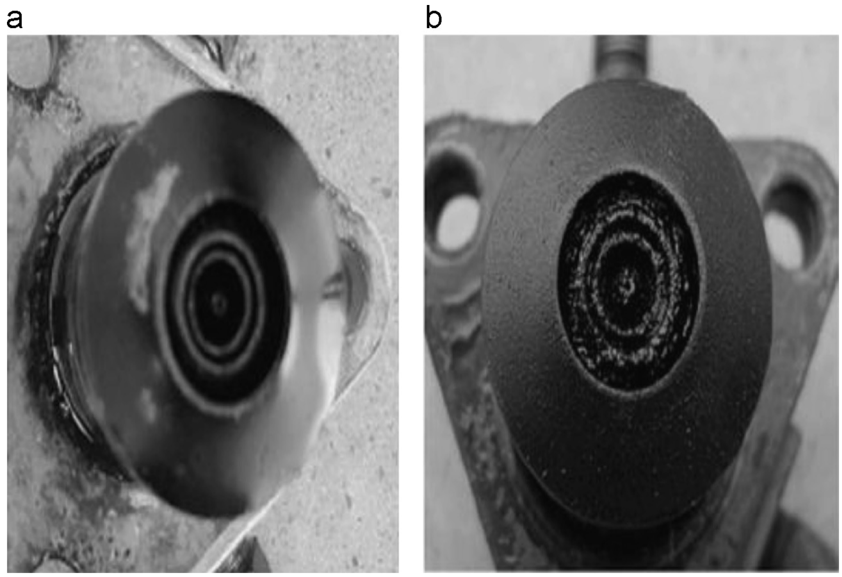


Fig. 5. Fuel nozzle (a) before and (b) after using trap grease.

Table 2
Properties of diesel and trap grease [27].

Summary of properties of diesel and trap grease			
Fuel	Experimental data		
	Density (kg/L)	Viscosity (cp)	Q_{HHV} (kJ/kg °C)
Diesel	0.816	5.0 (at $T=24$ °C)	45,170
Trap grease	0.910	7.0 (at $T=81$ °C)	38,718

but at the same time the octane number increases. They found that the 10% blending was optimal under various compression ratios of the engine, without requiring any modification(s) in the engine.

Bio-ethanol, produced from biomass, contains some ionic impurities like chlorides which enhance the conductivity of the alcoholic fuel. All engines are made up of metals which undergo corrosion by reacting with oxygen. As a result, a metal oxide layer is formed, which prevents further corrosion, by covering the metal surface. The halide impurities present in the bio-ethanol attack this passive oxide film resulting in pitting corrosion, and simultaneously produce aluminum hydroxide which can clog the fuel system. On the other hand, corrosion is also enhanced due to an increase in the electrical and galvanic conductivity. This problem can be overcome by maintaining very low concentrations of these impurities in the fuel. In addition to this, some corrosion inhibitors can also be added to the fuel. In cases where the fuel delivery system contains any polymers such as plastic or rubber parts, ethanol can attack the carbon–carbon bond in the polymers, or otherwise degrade the plastics, decreasing their tensile strength. Most of the car engines can tolerate up to 10% blend of ethanol in gasoline, without any serious damaging effects.

3.3. Glycerol

Glycerol is one of the most common by-products in various processes, and can be used as a source of carbon. Its bioconversion will directly benefit the environment by addressing the associated pollution problems and simultaneously relieving us from our dependency on petrol as an energy source. Glycerol can be converted into products like propane-diol, ethanol, etc. which are well known for their low CO_2 emissions [25]. A lot of research is going on to find more suitable microorganisms and enzymes which can convert the carbon in glycerol into more valuable compounds (Fig. 3).

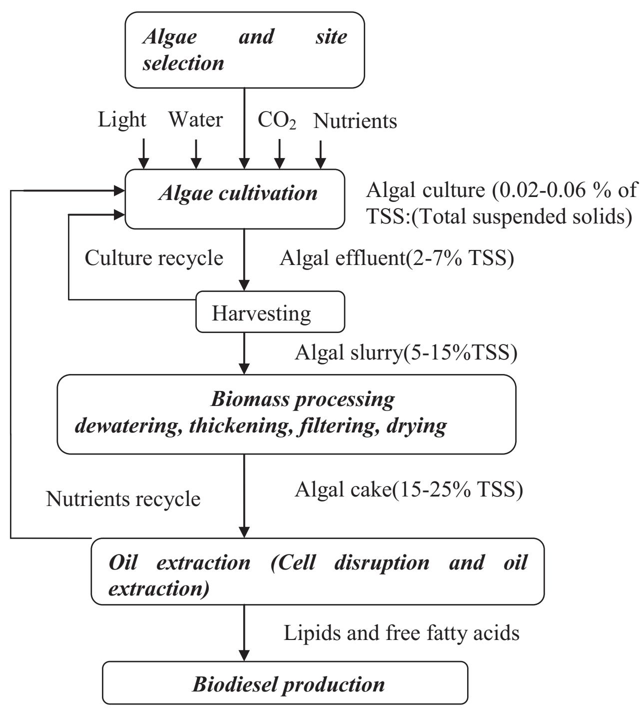


Fig. 6. Flowchart for biodiesel production [28].

3.4. Biodiesel

Biodiesel is one of the most promising future fuels, and can pose a serious competition to diesel or petrol in not too distant future. It comprises of mono-alkyl esters of long-chain fatty acids derived from vegetable oils such as palm oil, rapeseed oil, soybean oil, etc. Biodiesel is mainly produced from the rapeseeds; but palm seeds give a higher yield (Fig. 4). This, together with the low production costs involved in biodiesel production from palm seeds are two important factors which make it a good competitor for rapeseeds [10]. One of the major advantages of biodiesel is that it

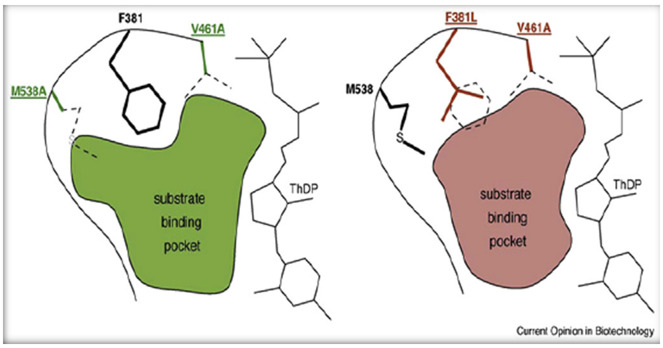


Fig. 7. A schematic stereo view of the active site of ketoisovalerate dehydrogenase (KIVD) [29]. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

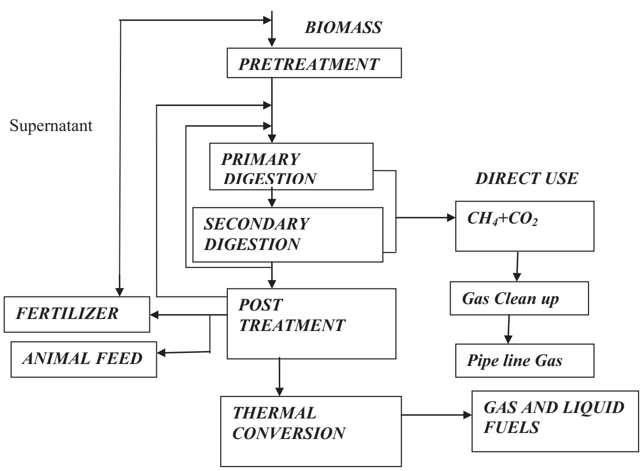


Fig. 8. Generalized anaerobic digestion process scheme.

can be used in an internal combustion engine without any modification(s).

In the year 2006, 6.5 billion L of biodiesel was produced globally. It is reported that nearly 75% of the total biodiesel production comes from the European countries. US spends around $5.5 billion to accelerate the growth of biofuel production. As a result, there was an increase of 1700% in two years and 450 billion gallons of biodiesel was produced in 2007.

The raw materials for the preparation of biodiesel can be classified into three types:

(i) Vegetable oils;
(ii) Waste frying oils, and
(iii) Animal fats.

Of these, waste frying oils are one of the best sources. Biodiesel with 4% fatty acid value can be prepared from waste frying oils by a two-step trans-esterification and purification process using ion-exchange resins. The biodiesel so produced meets the standards set by EN14214 (European standards set by European Committee for Standardization).

Waste trap grease oil is also used in the production of biodiesel. The waste trap grease is malodorous waste grease mainly from restaurant kitchen traps which are required for the minimum fouling of sewer lines. This grease is considered as a bio-oil fuel of sufficient heating value for combustion. It provides a way for waste management of grease, and is easy to transport, and also very cheap. One of the major problems is its chemical deposition after combustion (Fig. 5).

The trap grease oil is used in a gas turbine generator. The fuel system of a gas turbine is to be modified for dual fuel capability with a diversion valve and a heat exchanger with exhaust for elevating the temperature of trap grease. At a temperature of 80 °C, the trap grease has the same viscosity as that of diesel oil. Trap grease oil has lower NOx emissions, but higher CO and CO_2 emissions compared to those of diesel. The properties of trap grease oil and diesel have been compared by Al-Shudeifat and Donaldson [28].

The results are summarized in Table 2. Trans-esterification may be a suitable route to convert trap grease into a clean biofuel with a higher efficiency [27].

Biodiesel can also be produced from oil seeds or animal fats, but these approaches cannot meet the realistic needs. One major concern in case of use of oil seeds is that a large acreage of land is required to produce the large quantities of raw material required, whereas in case of animal fats a large capital is required to feed animals which will be used for raw oil production.

Considering these constraints, the use of oleaginous micro-organisms to produce the required raw material is considered to be a better alternative to the biodiesel production from oils. Oleaginous microorganisms which can be used for the purpose include algae, bacilli, fungi, yeast, etc. The overall process for producing biodiesel using algae is outlined in Fig. 6 [28].

Protein engineering is used to increase the catalytic efficiency resulting in an increase in the yield of biofuels. The production of proteins by all organisms follows a common fundamental process:

The central dogma consists of the following pathway:

$$\text{DNA} \xrightarrow{\text{TRANSCRIPTION}} \text{RNA} \xrightarrow{\text{TRANSLATION}} \text{PROTEINS}$$

DNA is a nucleic acid containing the genetic instructions used in development and functioning of all living organisms. It contains thousands of genes and carries the genetic information of the cell. Each gene serves as a recipe on how to build a protein molecule. Proteins perform important tasks in the cell, and regulate the functioning of the cell. Thus, every cell carries genetic information, and the DNA in the cell is duplicated to form a new DNA (replication). When proteins are needed, the corresponding genes are transcripted in RNA. The proteins are formed outside the nucleus of the cell. The structure of proteins is decided by the codes in RNA. This process is known as translation.

Global transcriptional machinery engineering creates a global change in metabolism in the organisms. It has been tested for *E. coli* and *S. cerevisiae* for improving bio-fuel production. By inducing a mutation in the transcription factor, the alcohol tolerance of the yeast is increased.

A mutant crp*(cyclic adenosine monophosphate (CAMP) receptor protein) is used to engineer *E. coli* for simultaneous utilization of glucose and xylose [29]. By developing a thoughtful protein engineering process, we can thus develop new efficient enzymes

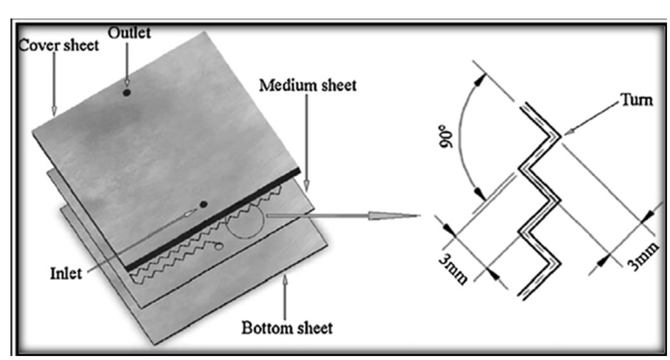


Fig. 9. Representative configuration of a zigzag micro-channel reactor [33].

which can hydrolyze biomass to sugars and then the sugars to biofuels. This technique has not been widely explored yet. One possible reason may be the limited sources of the enzyme. Metagenomics and single cell genomics may however be better alternatives for generation of biodiesel, as it is expected that by these new techniques there may be a rapid growth of enzymes resulting in a much larger increase in the production of biofuels.

Zhang and coworkers [30–32] engineered the active site of both ketoisovalerate de-carboxylate (KIVD) and 2-isopropylmalate synthase (IPMS) to accept large substrates to produce long chain alcohols, while on the same track metabolically engineered *E. coli* may produce both propanone and butanol.

In order to produce long-chain alcohols (C5–C8) from amino acid biosynthetic precursors, the active site of KIVD was modeled and altered to fit larger substrates (Fig. 7). The shaded areas are representations of altered binding pockets and those of double mutants M538A/V461A (green) and F381L/V461A (red), which offer less steric hindrance to larger substrates like 2-keto-4-methylhexanoate. Dotted side chains are wild type and highlight the changes in the substrate binding pocket as a result of mutations. ThDP is thiamine diphosphate, a cosubstrate.

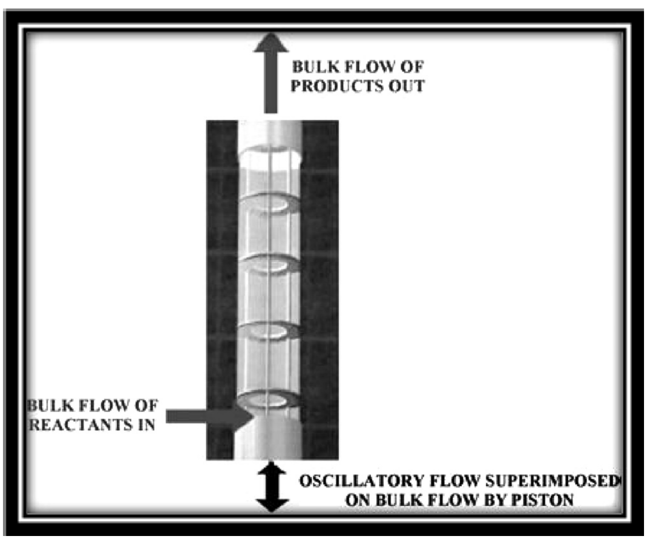


Fig. 10. Working of an oscillatory flow reactor [34].

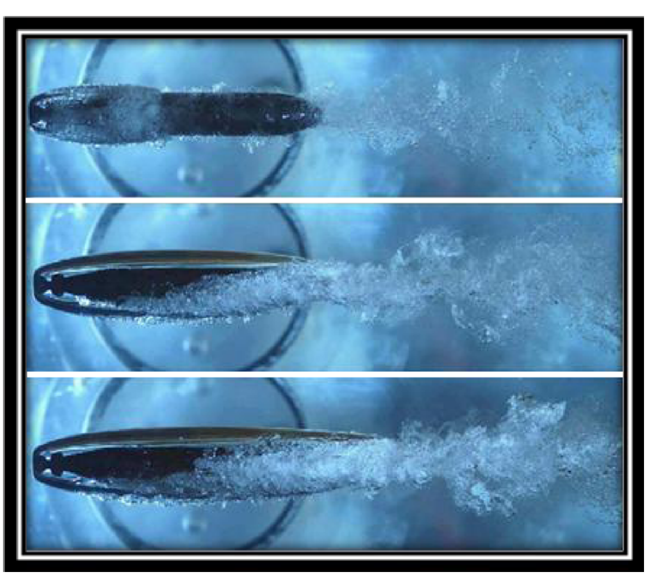


Fig. 11. Hydrodynamic cavitation [33].

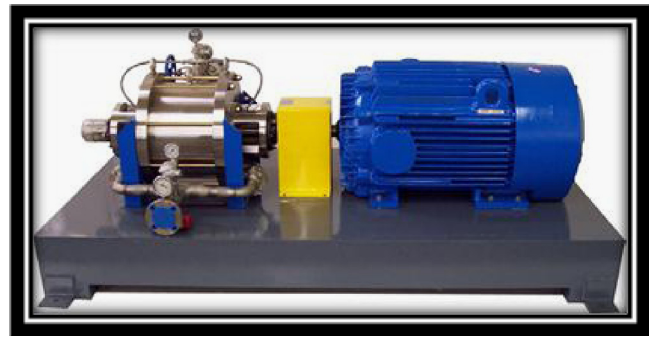


Fig. 12. A commercial SPR for biodiesel production developed by Hydro Dynamics, Inc. [35].

Biomass can be used to produce various fuels like methane gas or liquid fuels (Fig. 8), and can also provide a thoughtful way for waste management by digestion [29].

The processes for conversion of biomass into a renewable source of energy can be classified into following types:

(i) *Hydrotreating of crop oils*: in this procedure, the long chain fatty acids are first decarboxylated to get long chain alkanes. The resulting alkanes and alkenes then undergo thermal cracking to break the long chain alkanes into smaller chains. Some type of isomerization reactions may be there to produce the branched chains. The main disadvantages of the process are the requirement of external source of hydrogen and the lack of valuable by-products.
(ii) *Fischer–Tropsch process*: cellulosic biomass is converted into hydrocarbons' mixture using a gasification process.
(iii) *Rapid pyrolysis*: cellulosic biomass or other carbon containing feed stocks are subjected to a very high temperature pyrolysis at a very short residence time to partially gasify the stock.
(iv) *Transesterification*: this process involves catalyzed reaction of triglycerides with alcohol to produce biodiesel [3].

Transesterification is the most commonly used process for biodiesel production. It is a three step process in which first triglycerides are converted into diglycerides, then into monoglycerides, and finally into glycerol and biodiesel. The technique of transesterification of vegetable fats with alcohols in presence of an alkaline catalyst has already been commercialized for preparation of biodiesel. However, the crude biodiesel obtained from simple transesterification has a number of impurities and is not a remarkable fuel. A membrane reactor is introduced to get biodiesel of higher purity. Though the use of a membrane reactor decreases yield of biodiesel, it also decreases the difficulties encountered during the purification of biodiesel [33].

The use of heterogeneous catalysts and enzymes has helped improve the quality and quantity of biodiesel produced from those oils having large contents of free fatty acids, while for other sources homogeneous catalysis is preferred. Heterogeneous catalysis poses the problem of mass transfer limitations, due to which it is still quite far from the stage of commercialization. Newer technologies are coming upfront which have the capacity to increase the rate of trans-esterification beyond what is possible in a static reactor. Some of these are described in the following section.

3.4.1. Increasing the efficiency of transesterification

3.4.1.1. Micro-reactor. A micro-reactor, with a zigzag pathway, significantly increases the rate of production of biodiesel. It is capable of producing small drops with a large specific surface/

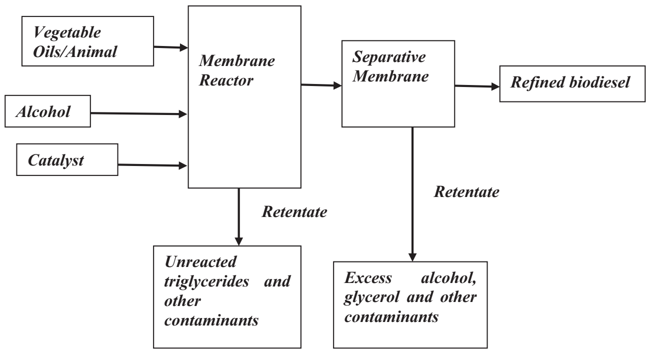


Fig. 13. Working of a membrane reactor [37].

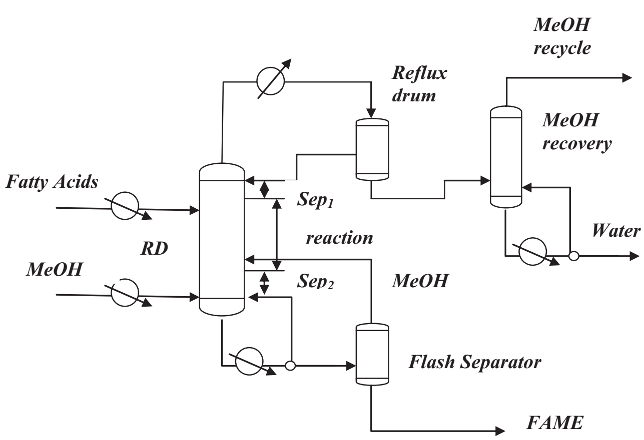


Fig. 14. Fatty acid methyl esters (FAMEs) production by esterification with methanol in a reactive distillation column (RDC) [33].

interfacial area, and consequently the attainable yield of the product also increases. The yield of methyl ester has been found to reach up to 99.5% in a zigzag micro-channel reactor using 9:1 M ratio of methanol to oil while the catalyst was only 1.2% [33]. It is also reported that a lesser amount of energy is required in a microreactor, for the preparation of the same amount of biodiesel, than in a conventional reactor, i.e., a stirred tank reactor (STR) (Fig. 9).

3.4.1.2. Oscillatory flow reactor. These are tubular reactors provided with equally spaced orifice plate baffles which produce oscillatory flow using a piston drive. When the liquid enters the reactor, the oscillatory motion causes a radial mixing resulting in an increase in mass and heat transfer. Generally, an oscillatory reactor has a large aspect (length-to-diameter) ratio. Harvey et al. developed a new oscillatory reactor which consisted of two vertically positioned jacketed tubes of 1.5 m length and internal diameter of 1.5 mm, (Fig. 10), and a conversion of 99% was obtained within 30 min using a ratio of methanol to rapeseed oil as 1.5 in the presence of sodium hydroxide as a catalyst [34]. The large length to diameter ratio decreases the capital cost [33].

3.4.1.3. Cavitational reactor. These reactors use acoustic energy or flow energy to generate cavitation phenomenon. Firstly, the pressure changes, from sound and flow, result in violent collapse of cavities which generate large amounts of energy over a small region. Cavitation causes the intensification of the process by generation of local turbulence and liquid micro-circulation. A conversion of 90% was obtained within 15 min for trans-esterification of vegetable oils. It has been reported that these types of reactors are about 140 times better than the conventional STR (Fig. 11) [33].

3.4.1.4. Shock power reactor (SPR). SPR also works on the principle of cavitation, and the only difference is in the method of producing cavities. A feed is charged into the reactor and passed through the generator's spinning cylinder. The specific geometry of the cavities inside the cylinder and rotational speed create a pressure difference within the liquid where tiny bubbles are formed. The cavitation is controlled in such a manner that the bubbles collapse only inside the cavities and away from the metal surface. The shock waves increase the surface area of the phases, and it takes only a few seconds for the completion of the trans-esterification process (Fig. 12).

3.4.1.5. Rotating spinning tube reactor. These reactors consist of two tubes with diameter of one tube slightly greater than the other. The tube with smaller diameter rotates rapidly within the larger tube and there is a very small annular gap between the two tubes. Once the reactants are introduced into the reactor, Couette flow is introduced and the two liquids mix instantaneously and move through the gap as a coherent thin film. This type of flow leads to a large mass transfer within a short time, and a three-fold increase in the rate of reaction is reported. Lodha and Jachuck used this reactor, and found a conversion of 98% within 40 s [36].

3.4.1.6. Micro-wave reactor. Micro-wave reactors use the micro-wave radiation to transfer energy directly to reactants and thus increase the rate of reaction. A higher conversion is achieved in a given time in comparison to that in conventional (SPR) reactors. For the mixture of vegetable oil, sodium hydroxide, and methanol, all consisting of polar and non polar parts, the micro-wave radiation may be used for fulfilling the energy requirements. A conversion of more than 97% is achieved within 2 min for the trans-esterification reaction.

3.4.1.7. Membrane separation reactor. This technology is used to obtain high yields of biodiesel. It can also affect the equilibrium of the reaction, and makes it possible to monitor the rate of production of a given compound. It is reported that biodiesel is better than petrol or diesel in terms of the free sulfur content, biodegradability, density, flash point, and aromatic content. Biodiesel reduces the net carbon dioxide emissions by 70% when compared to the conventional diesel fuel (Fig. 13) [37].

3.4.1.8. Reactive distillation. Reactive distillation combines chemical reaction and product separation in the same unit. To obtain high yields of a product, a large amount of alcohol is required as the reactant; but then the recovery of this alcohol is a problem which can be solved by distillation within this reactor. The upward moving vapors of methanol act as an agitator and serve the purpose of achieving a uniform mixing. Generally, a ratio of 6:1 of methanol to oil is used, but in this reactor a ratio of 4:1 with KOH as the catalyst can achieve the conversion of 95% in 3 min (Fig. 14).

In spite of all the advances in biodiesel production, much work still needs to be done to make biodiesel compete with diesel or petrol [38].

3.4.2. Problems with biodiesel

The main problem with the use of biodiesel is its oxidation and polymerization occurring during combustion or storage. Due to these reactions, the biodiesel becomes acidic, and forms gum-like sediments which can plug the fuel filters. Due to the presence of unsaturation in the parent fatty chain, the double bond reacts with

oxygen as soon as it is exposed to air. The oxidation process is influenced by various factors like light, temperature, extraneous metals, peroxides, and the surface area between air and biodiesel. The problems due to oxidation of biodiesel can be tackled by addition of some kinds of antioxidants, or alternatively the fatty chain may be modified [37].

3.5. Hydrogen

The use of hydrogen for providing energy is not new. Studies for assessment of the potential of hydrogen as an alternative fuel had been started since World War II. Until the 1960s, it was used in many countries for the purpose of street lighting and for domestic use such as cooking, heating and household lighting. The oil crisis in the 1970s was a major factor in promoting the use of hydrogen as an energy provider. However, real interest in large scale use of hydrogen was generated in the late 1990s with major breakthroughs in fuel cell technology. It was found that it can be used as a compact energy source in fuel cells and batteries. In addition to this, it is envisaged that in the near future, with growing concerns regarding the generation of Green House Gases (GHG's) by the conventional fossil fuels used presently in the transportation sector, hydrogen will become very popular as a transport fuel because it is considered to be virtually emission free at the point of final use [39].

3.5.1. Properties of hydrogen

Hydrogen is the lightest of all elements and is considered to be a primitive substance from which all matter and other elements have evolved. It is found in three isotopic forms: protium (or hydrogen) with an atomic mass 1.0079, deuterium with a mass of 2.0142, and tritium with a mass of 3.0144. In natural hydrogen, 99.985% is protium and 0.015% deuterium. Tritium is an unstable radioactive element with a half-life of 12.26 years.

Hydrogen comprises of more than 75% of matter in the universe. In nature, it occurs in combination with other elements. The most abundant source of hydrogen is water (containing 11.2% by weight of hydrogen), biomass (containing varying amounts of hydrogen, depending upon the nature of biomass), natural gas and coal. For hydrogen to be used as a fuel, it must be obtained as free hydrogen from these resources. It has the lowest molecular weight which gives it extreme properties such as high thermal velocity and conductivity and lowest viscosity and density. It has very low ignition energy and a wide flammability range. These properties, especially the high heat of combustion and low molecular weight of the product gases have made hydrogen a fuel of choice for rocket propulsion.

Hydrogen can be converted to the liquid form for convenience in storage, use and transport. Liquid hydrogen is colorless in nature with a liquefaction temperature of 20.3 K. It can be stored in containers, pumped through pipelines, metered, and restricted by valves of usual design [40].

Among known fuels, hydrogen has the highest energy content per unit of weight. When burnt in an engine, it produces effectively zero emission and in case of powering of a fuel cell, water is its only waste [40]. All these properties of hydrogen, combined with the fact that combustion of hydrogen does not produce the greenhouse gas, namely carbon dioxide will make hydrogen a popular alternative fuel of the future.

However, there is one more aspect related to the use of hydrogen as an alternative to conventional fuels that should be given a very serious thought. Hydrogen is one of the two natural elements that combine to make water. It is one of the most plentiful elements on earth, and has an immense potential of becoming the energy carrier that will fuel our culture far into the future, if it could be produced in a cost-effective manner in the short run and if it is not lost from our planet in the long-term scenario. The last part of the last statement must be taken in the spirit of a very important historical statutory warning, with no less implication than the possibility of extinction of the entire life on our lonely planet. Water has probably existed on many heavenly bodies, with the most recent proof coming from the investigations of “Curiosity” on Mars. And, we have very little evidence for its present-day existence on other planets or their satellites. If in the known universe, there is a tendency for water to leave its host in the long run it becomes even more critical that our human interventions ought not result in acceleration of that process especially because no chemical process or operations of storage, handling and transportation are one hundred percent efficient either from the conversion or leakage points of view, respectively. Life on earth in all likelihood would be a very sensitive function of the amount of water present on it, and even a small percentage depletion might result in an irreparable and irreversible damage to this unique, or at least very rare, existence of consciousness.

This seemingly over-cautious philosophy must be the corner-stone of all hydrogen-economy initiatives of all governments in the present or in the future. We owe it to the posterity that present human greed does not lead to the vanishing of the human future. Time scales involved might become a subject of scientific debate, but errors of calculation in this delicate play with nature might be potentially too risky even to attempt their practice. We, especially the senior author of this chapter, consider it our utmost obligation to voice this grave concern over the possibility of such a significance which no one else seems to have even imagined so far. Looking back, it could be incomparably worse than the creation of the global warming effects of our historical choice of petroleum economy. We are at the cross-roads of an immense significance, and a mistake here and now could well be tantamount to unplugging of all life on earth!

Should these concerns be wrong, hydrogen does have a number of advantages to make it an attractive alternative fuel.

3.5.2. Hydrogen storage

Despite all advantages of hydrogen, storage of hydrogen is regarded as one of the most critical issues, which must be resolved before a technically and economically viable hydrogen-fuel system can be established. Considerable progress concerning hydrogen-propelled vehicles has been achieved over the past few years, wherein most of the developmental efforts have concentrated on the propulsion system and its vehicle integration. However, there is a general agreement in the automotive industry that the on-board hydrogen storage is one of the most critical aspect that needs to be addressed before hydrogen is used commercially in the future car fleets. Till now, no approach exists which is capable of fulfilling the technical requirements for a range greater than 500 km while meeting all the performance parameters regardless of costs. The physical limits for the storage density of compressed and liquid hydrogen have nearly been reached. But there is still a potential in the development of solid materials for hydrogen storage such as systems involving metal hydrides and Metal Organic Frameworks (MOFs) [39].

3.5.3. Hazards

3.5.3.1. Compressed hydrogen (CH_2). Compressed hydrogen presents exactly the same hazards as any other compressed gas, and therefore will have all the potential hazards same as of Compressed Natural Gas (CNG). However, there are two other hazards with hydrogen, namely its small molecular size, and its minimum ignition energy (MIE). The small molecular size means that hydrogen will easily diffuse out of a system which is completely leak-tight to other gases. It can also induce sweltering and cracking of steels at elevated temperatures. Hydrogen also has a much lower MIE than any traditional

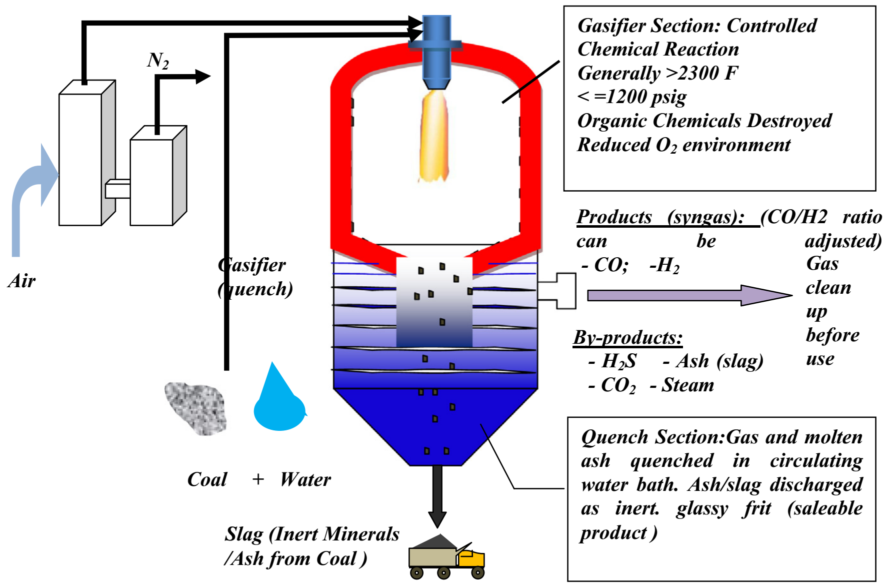


Fig. 15. Overview of gasification process [47].

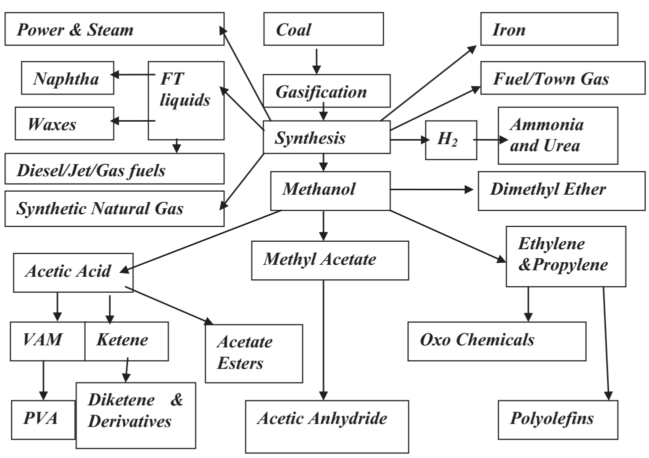


Fig. 16. Different FT products from syngas.

hydrocarbon fuel, at 0.017 mJ, as opposed to a value nearer to 0.2 mJ for a hydrocarbon [1]. This makes hydrogen far more sensitive to ignition than any other gaseous fuel.

There are some references to hydrogen having a positive Joule–Thompson coefficient. A large reduction in pressure (which occurs during a leak from a high-pressure system), therefore, results in a rise in temperature, rather than a fall, due to the expansion [41]. Hydrogen also has a much higher flame speed than any other gas; it has wider limits of flammability, and also detonates readily. An ignition of hydrogen may result in a higher overpressure than the leakage of the same mass of any other fuel in a confined place [42]. Thus, hydrogen presents different and additional hazards when compared with the traditional fuels. Although hydrogen readily disperses due to its very low molecular weight and low density, it may detonate even if not confined. This will produce overpressure effects much greater than those of any traditional fuel.

3.5.4. Liquefied hydrogen (LH_2)

Liquefied hydrogen boils at about 20.3 K, at atmospheric pressure, and is stored at about that temperature, but under a nominal pressure to minimize the boiling [43]. It has a nominal density of about 0.0077 kg m^{-3} at its triple point of 13 K [44]. Clearly, many of the flammability aspects of LH_2 are the same as those of compressed hydrogen, but the low storage temperature adds more hazards. It is below that of the freezing point of both oxygen and nitrogen, so there is the potential for solid oxygen or nitrogen to form in a LH_2 system. Also the maximum temperature excursions that a storage system would undergo from an ambient temperature of about 40 °C to the storage temperature of about 13 K amounts to a difference of about 300 °C. This imparts high thermal and mechanical loads on the pipework, vessels, and flanges, and the cool-down has to be controlled to minimize the potential for leakage due to uneven contraction of the system. This will also apply to gaskets and seals. Liquefied hydrogen has the potential problem of causing hydrogen embrittlement of metallic components in the system. This can, however, be countered by using appropriate materials of construction. LH_2 spillages are of a different nature as the gaseous hydrogen readily disperses in the open air due to its extremely low density. The liquid spilled being extremely cold, any spillage rapidly evaporates and cools the ground onto which it falls. This produces a rapid “puff” of expanding vapor which rises rapidly and disperses. The high turbulence generated by the sudden expansion of vapor from the liquid mixes hydrogen with air, and the gas cloud typically expands by a factor of five [45]. It is expected that as LH_2 has similar effects as Liquified Natural Gas (LNG), an explosion may occur if LH_2 is spilled onto water.

3.6. Coal: Coal to Liquid Fuels (CTL) technology

Coal liquefaction, Coal to Liquid or CTL, is the conversion of solid coal into liquid fuels and chemicals. It mainly consists of breaking down coal's molecular structure, and addition of hydrogen. There are two routes which have been taken so far to achieve this—the direct coal liquefaction (DCL), and the indirect coal liquefaction. While direct coal liquefaction consists of direct hydrogenation of coal, indirect coal liquefaction breaks down coal into CO and H_2 through gasification followed by conversion of CO and H_2 into liquid products by Fischer–Tropsch (FT) process. Both the processes are carried out at high temperatures and pressures in presence of catalysts. The indirect coal gasification is discussed in detail in the following sections.

3.6.1. Gasification of coal

Coal is blown through with oxygen and steam, while being heated and pressurized. Care is taken to ensure that the supply of

oxidizer is insufficient for complete combustion. The reactions produce a gaseous mixture of carbon dioxide (CO_2), carbon monoxide (CO), water vapor (H_2O), and hydrogen (H_2). Some by-products like tar, phenols, etc. are also possible. This process has been conducted in-situ within natural coal seams (referred to as underground coal gasification) and in coal refineries (Fig. 15). The main product here is syngas, (H_2+CO), and the main reaction involved is:

$$3C+O_2+H_2O \rightarrow H_2+3CO$$

Conditions: *T*: 600–900 °C; *P*: 30 atm; Catalyst: (oxides and chlorides of alkali metals: NaCl, KCl) [46].

Syngas is then passed through a Fischer–Tropsch (FT) reactor to produce alkanes, such as in natural gas, gasoline, and diesel fuel. If hydrogen is the desired end-product, coal gas undergoes water–gas-shift reaction where more hydrogen is produced:

$$CO+H_2O \rightarrow CO_2+H_2$$

Conditions: *T*:1000 °C; *P*: 30 atm; Catalyst: Iron Oxide.

3.6.2. Fischer–Tropsch process

The Fischer–Tropsch process involves the following chemical reactions:

$$(2n+1)H_2+nCO \rightarrow C_nH_{(2n+2)}+nH_2O$$

where 'n' is a positive integer. Mostly, straight-chain alkanes and some branched alkanes are formed. Some alkenes, as well as alcohols, and other oxygenated hydrocarbons are also formed in the process.

Several reactions are involved in obtaining the gaseous reactants required for the FT catalysis. Any sulfur present in the reactant gases needs to be removed, as it can readily poison the catalysts. Water–gas-shift reaction, wherein hydrogen is generated, is as mentioned earlier:

$$H_2O+CO \rightarrow H_2+CO_2$$

If the FT plant starts with methane, it is first converted to carbon monoxide and hydrogen by the following reaction:

$$H_2O+CH_4 \rightarrow CO+3H_2$$

There is a huge list of components which can be produced from the syngas as shown in Fig. 16.

3.6.2.1. Process conditions. Fischer–Tropsch process needs to be operated in the temperature range of 150–300 °C (302–572 F). Though higher temperatures lead to faster reactions and higher conversion rates, those result in an increased methane production. The temperature, therefore, needs to be maintained at low permissible levels. Increased pressure favors the more desirable higher conversion rates, and the long-chained alkanes' formation. Typically, pressures range from one to several tens of atmospheres. The upper limit of pressure is only dictated by the cost of the equipment.

A variety of synthesis-gas compositions can be used. For cobalt-based catalysts, the optimal H_2:CO ratio is around 1.8–2.1. Iron-based catalysts promote the water–gas-shift reaction, and thus can tolerate significantly lower ratios. This reactivity can be important for synthesis gas derived from coal or biomass, which tend to have relatively low H_2:CO ratios (<1).

3.6.2.2. Product distribution. In general, the product distribution of hydrocarbons formed during the Fischer–Tropsch process follows an Anderson–Schulz–Flory distribution [48], which can be expressed as

$$W_n/n=(1-\alpha)^2\alpha^{n-1}$$

where W_n=weight fraction of hydrocarbon molecules containing 'n' carbon atoms, α=chain-growth probability, or the probability that a molecule will continue reacting to form a longer chain. α is mostly determined by the catalyst, and the specific process conditions.

The formation of long-chain hydrocarbons increases upon increasing α. Long-chain hydrocarbons, e.g., waxes, are mostly solid at room temperature. As a result, the production of liquid transportation fuels requires cracking of the FT products. Extensive reviews on catalytic gasification of coal are available [49,50]. These catalysts with fixed-sized pores control the length of the carbon chains being formed (usually $n<10$). Methane formation can therefore be reduced while at the same time controlling the formation of long-chain hydrocarbons. But, the efforts in this direction have seen minimal success thus far.

3.6.2.3. Fischer–Tropsch catalysts. Cobalt, iron, and ruthenium are the highly preferred catalysts though there are many others that suit the purpose. Cobalt seems to be the most active catalyst, while iron suits best for low-hydrogen-content synthesis gases. But cobalt is very sensitive to poisoning due to sulfur traces. Apart from the active metal, the catalysts may also contain "promoters," like potassium and copper. High-surface-area binders/supports such as silica, alumina, or zeolites support the catalysts. The choice of catalyst also depends on the type of feedstock. For instance, while cobalt catalysts are best suited for natural gas, iron catalysts are better for coal/biomass.

Among the commonly used catalysts, iron poses a problem due to the formation of oxides or carbides during the reaction. It becomes crucial to control these reactions as it may adversely affect the life of the catalyst particles. Nickel results in methane formation, and hence is mostly avoided.

3.6.3. Storage and transportation

The infrastructure established for distribution and storage of petroleum is very much compatible with CTL fuels as well [51]. Hence, there would be no requirement for new or modified pipelines, storage tanks, or retail station pumps.

3.6.4. Recent R&D activities in CTL technology

(a) CO_2 sequestration
Recently there has been much concern over CO_2 sequestration since almost 50% of carbon in coal is converted to CO_2 which has purity as high as 98% [52]. This makes it readily applicable for further utilization as in CO_2 sequestration.

(b) Chemical reaction engineering challenges in coal liquefaction
In spite of the advances in DCL and Fischer–Tropsch Synthesis

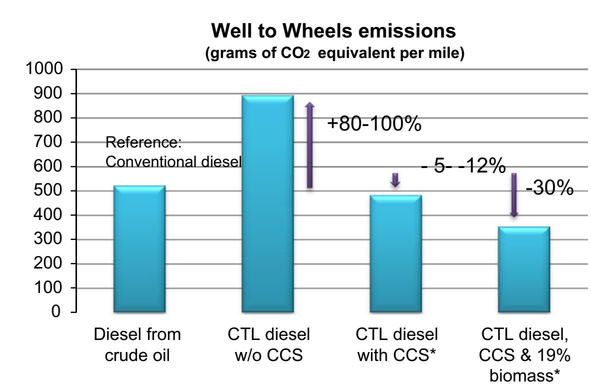


Fig. 17. Well to wheels emissions [53]. *CCS=carbon capture and storage.

(FTS), owing to the lack of chemical reaction engineering data DCL is still in a relatively immature stage with challenges remaining unsolved in almost every aspect of the process [52]. In addition, the increasingly stringent specifications for transportation fuels and environmental requirements for waste management and CO_2 sequestration demand more research and development. Some of the problems include:

- Low thermal efficiency of CTL of about 45–55%.
- Being exothermic reactions, DCL and FTS release huge amounts of heat—almost 20% of the heat of combustion of the product. Controlling the reaction temperature while employing an optimal use of the reaction heat is a major challenge here [52].
- Pressurized gasifiers with a large throughput and suitable product composition are important for higher thermal efficiency of coal-liquefaction processes.

(c) Challenges in DCL

Poor mixing of the three phases (gas, liquid, and solid) in the slurry-phase reactor, results in coking and settling of solid particles at the bottom of the reactor, which would require a heavy duty pump for recirculation [51].

According to "Coal liquefaction—A research and development needs assessment, 1989" [51] following are the challenges in DCL:

- Identification of structural changes in coal during heating in slurry and correlation thereof with the free-radical-fragments' generation.
- Understanding the catalysis and kinetics of the reactions in order to design better catalysts.
- Understanding the kinetics of hydrogenation of free-radical fragments of coal in order to check the reactions proceeding in the reverse direction.
- Modeling and simulation of the reaction mechanism and transport behavior in order to increase the conversion rates, throughput, and separation of the liquid–solid at the product end. Currently, the flow and concentration profiles of various substances inside the reactor are completely unknown which makes design as well as process control very difficult. Such an understanding would also provide a great deal of insight into the reactor behavior.
- Designing and modeling the high-throughput liquefaction reactor and slurry pre-heaters.
- Improving product-separation technique especially for liquid and solid and for chemical production.
- Better system integration for lesser power consumption, wastage, and other utilities, as well as for a higher efficiency.

(d) Challenges in FTS

Gasification is a major cost in FTS, with oxygen generation, CO_2 and H_2 separation units all being of very high costs. An equally challenging issue is the separation of the catalyst from the slurry medium which depends on the size distribution and stability of the catalyst, flow behavior of the slurry, apart from the design of the reactor. It is also crucial to further process the wide range of FTS products such as light hydrocarbon gases, paraffinic waxes, and oxygenates, in order to produce high-quality diesel and gasoline.

The challenges in FTS can be summarized as [51]:

- Developing a low-cost technique for O_2, CO_2, and H_2 separation.
- Pursuing higher conversion efficiencies coupled with low methanation at high temperatures through design of better catalysts. It would also be possible to recover energy through efficient catalysis.
- Designing better reactors, understanding the flow of slurry, and studying the stability of the catalysts for better separation of catalysts from the slurry.

3.6.5. *Why CTL?*

3.6.5.1. Environmental impact. Though the carbon emissions of CTL are high, there are several ways to mitigate these emissions. Re-engineering the processes, and coupling CTL with carbon capture



Fig. 19. A photograph of a micro-explosion [54].

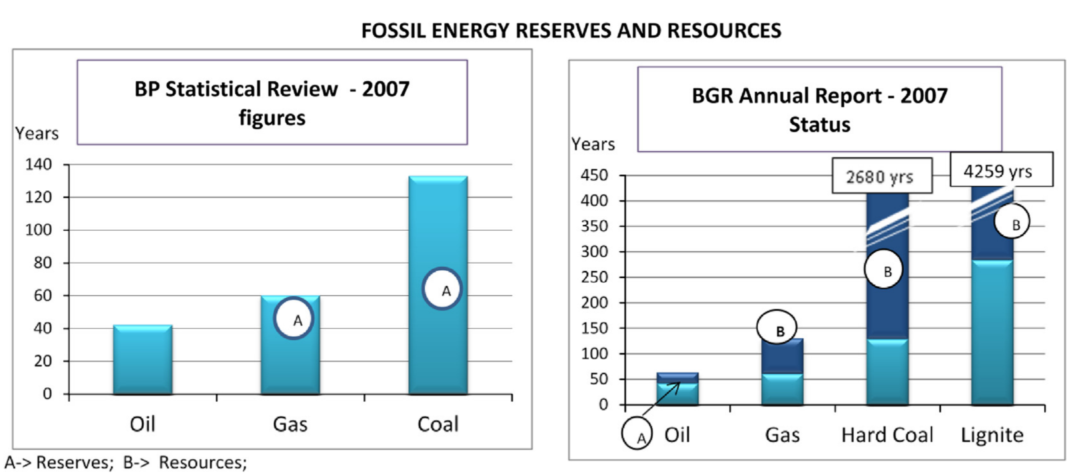


Fig. 18. Fossil energy reserves and resources (worldwide) [53].

and storage (CCS) or with algae-based processes are some of the options [50]. It is important to note here that the carbon emissions of a fuel produced in a CTL plant equipped with CCS are equivalent to those of a conventional fuel produced from crude oil. As reported in a study in 2009 by the US Department of Energy, there is a decrease of 5–12%, depending on the nature of investment. Since CO_2 from CTL plants is free of nitrogen, purification costs are reduced or avoided. Carbon dioxide produced in this way can also be used for enhanced oil recovery (EOR), thus adding to its commercial value (Fig. 17).

3.6.5.2. Depleting fossil energy reserves. As shown in Fig. 18, the depleting crude oil and gas reserves, and the abundantly available coal resources worldwide is another driving factor for CTL [53].

Other advantages of FTS fuels may be stated as follows:

(a) These fuels are compatible with today's diesel- and gasoline-powered vehicles.
(b) There is no need for change in infrastructure for distribution or storage (pipelines, storage tanks, or retail station pumps) in case of a shift over from petroleum to CTL fuel.
(c) Fischer–Tropsch (FT) diesel may provide similar or better vehicle performance when compared to the conventional diesel.
(d) Owing to the near-zero sulfur content, Fischer–Tropsch diesel is expected to reduce the emissions from a variety of diesel engines and vehicles. This property can enable the use of advanced emissions-control devices. The benefits of the FT fuel over the conventional fuel, as estimated by the US Environmental Protection Agency based on the inherently cleaner-burning characteristics of FT diesel, are summarized in “Clean Alternative Fuels” as:
(i) Nitrogen-oxides' reduction, and even further reductions with the addition of emissions-control catalysts.
(ii) Low sulfur and aromatics contents give almost-zero or very little particulates' emissions.

4. Attempts to increase the efficiency of conventional fuels

4.1. Water-in-oil emulsions

It is a surprising fact that water, which is a well known agent for inhibiting combustion, can actually increase the rate of combustion. The addition of water to diesel increases its combustion efficiency in the combustion engine. Water can work better with diesel in comparison to all other fuels like gasoline or vegetable oils. Moreover, addition of water to diesel has been found to decrease the emissions of nitrogen and sulfur oxides in the exhaust. The emulsified fuels give a lower percentage of polycyclic aromatic hydrocarbons in flame, as well as reduced emissions to the atmosphere. Addition of water to dodecane fuel decreases the formation of soot. This decrease is mainly up to 5% of water addition. A further increase in water content of the emulsified fuel does not affect soot formation. It has been found by viewing through a Charge Coupled Device (CCD) camera that the soot is mainly formed in the central axis of flame. With the addition of water, the time of contact of the fuel and air increases [12]. The increase in the time of contact may be contributed due to the better mixing of air and fuel, or decrease in flame temperature, or both. Hence, it results in a more complete combustion and a decrease in the soot formation. It is also observed that it is not the amount of water that reduces the coke in soot, but rather it is the interfacial area between water and fuel that is effective. If the droplets are smaller, the amount of soot further decreases. Hence, the inclusion of a good surfactant, which can decrease the surface tension and increase the interfacial area, is vital. The nature of surfactant thus affects the combustion properties of an emulsion fuel! A probable reason for the increase in combustion efficiency is that when the mixture of water and diesel is preheated, due to its high volatility, water evaporates and results in an explosion in the continuous phase of hydrocarbon. This phenomenon occurs at a much higher temperature than the boiling point of water, i.e., approximately at 270 °C. It is known as a micro-explosion, and this helps in atomization of the fuel (Fig. 19).

The phenomenon of micro-explosion is thus beneficial for a better in-situ mixing of the fuel and air, and results in the increase in combustion efficiency of the fuel.

4.2. Double emulsions

Besides these emulsions, studies on double emulsions (oil/water/oil) are also going on [12]. In spite of the fact that double emulsions have higher viscosities, they do not pose any real problem in fuel formulation. The double emulsion gives lower NOx and CO contents in the exhaust, and a high exhaust-gas temperature.

It was found that the addition of diglyme improves the combustion characteristics, but also imposes a problem of fuel stability. Actually, diethyl glycol dissolves in water phase, and makes it a better solvent for the surfactant which desorbs from the interface of oil and water resulting in the instability of the emulsion. This effect is less pronounced in a double emulsion, and hence diglyme can be safely used in double-emulsion systems to increase the combustion efficiency of the fuel.

4.3. Microemulsions

Microemulsions of diesel and water [12], and gasoline–alcohol–water [55] have also been studied with regard to the various characteristics of fuels. Microemulsions lead to lower concentrations of NOx and CO in the exhaust gas, and also better combustion characteristics notably including lower concentrations of unburnt hydrocarbons and in case of gasoline no detectable particulates in the exhaust gas. One big challenge however is to reduce the cost of formulation of microemulsions, and it is a well known fact that the microemulsion formation requires higher loadings of surfactants. Extensive research is still to be done in this field, which at present is at best only in its infancy [12].

5. Economic evaluation of alternative fuel technologies

Though the alternate fuels have a number of advantages over the conventional fuels, especially environment related advantages, they still have a long way to go before they can be considered as economically viable alternatives to the conventional fuels presently used. A lot of research efforts are currently being directed towards analyzing and improving the economic viability of these fuels. The various economic aspects for some selected alternative fuels are considered in this section.

The transportation sector has been the focus of economic analyses and cost comparison studies for conventional versus alternative fuels, as it is considered to be one of the most polluting sectors responsible for GHG generation, resulting in global warming. Bioethanol is emerging as an important alternate fuel in the transportation sector because of its ease of blending with gasoline and the advantages that this blend offers. Bioethanol, blended with gasoline (E85: containing up to 85% ethanol) has been used in Flexible Fuel Vehicles. Though this blend has lower emissions of GHG's, its commercial acceptability is reduced by the fact that it has a lower fuel economy; E85 has about 27% less energy per gallon than gasoline [57]. However, ethanol being

a high octane fuel, offers increased vehicle power and performance. Thus, improvements in engine design and advances in control and combustion systems are likely to significantly increase the demand for bioethanol in the transportation sector. In spite of a number of robust microorganisms being discovered/engineered for production of bioethanol through the fermentation route, the initial costs of pretreatment of the biomass and the costly cellulose enzymes required for fermentation, especially to improve the yield, the production costs of bioethanol produced by fermentation remain way higher than the local costs of gasoline [56]. Continuous efforts towards improvements in pretreatment techniques and bio-engineering of microorganisms and enzymes, used in fermentation, are likely to reduce this gap to a significant extent.

Though biodiesel is gradually catching up with conventional diesel and petrol in terms of its use in applications such as internal combustion engines, it has yet to reach its full commercial potential, especially in the developing countries. Vegetable oils serve as the major feedstock for the production of biodiesel. Virgin vegetable oil contributes to 70–95% of the total biodiesel production cost [58]. Comparative techno-economic analysis has shown that the cost of biodiesel from waste cooking oils is lower than that of fresh oils. Further, Araujo et al. [58] carried out an economic assessment of biodiesel production from waste frying oils. They proposed that improved logistics would play an important role in the reduction of cost of production of biodiesel from waste biomass such as used frying oil. Ong et al. [59] carried out a life-cycle cost analysis and found that the life-cycle cost for 50k t of palm biodiesel production plant with an operating period of 20 years is $665 million, with a payback period of 3.52 years. Providing even marginal fiscal subsidies is likely to bring the palm oil derived biodiesel costs at par with the fossil fuel costs. Globally, biodiesel production increased from 8.4 million t in 2007 to 20 million in 2010. It is expected to reach 150 million t by 2020. However, feedstock variability and production capacity limitations have largely affected the economic viability of biodiesel. The main hurdle in production of biodiesel from vegetable oils is that it uses fertile lands which could have otherwise been used for production of food crops. This concern can be mitigated by using microalgae as feedstock for production of biodiesel. As opposed to terrestrial plants, microalgae do not require soil fertility or fresh water; these are also free from dependence on solar radiation and other seasonal variations affecting biodiesel production. In addition, microalgae have an energy efficiency about 5 times greater than that for terrestrial plants. Though microalgae have a faster growth and high lipid-to-biodiesel yield, the economic profitability needs to be further improved before it can be considered as an economically viable alternative to other biodiesel feed stocks [60].

The major concern in commercialization of CTL technologies is the large amounts of CO_2 emissions which will add to the existing GHG burden caused by the conventional fuels. Hence, CTL technologies such as Fischer–Tropsch processes have been integrated with carbon capture and storage (CCS) technologies. The techno-economic evaluation of these technologies has been done in order to bring these technologies closer to commercially viable alternatives to conventional fuels, and simultaneously taking care of the negative environmental impact that these may produce [61,62]. The studies show that considering the high capital costs involved, investments in CTL plants carry a significant financial risk. A CTL plant adapted for co-production of electricity is costlier than a liquids-only plant; however, the additional revenue generated by the sale of the electricity produced, can significantly lower the cost of the liquid products. On similar lines, concepts such as biodiesel bio-refinery improve the economics of the process by promoting process conditions that favor co-production of costly products such as succinic acid. This strategy can enhance the profit of the bio-refinery by 60% for a 20-year plant lifetime [63].

Although the alternative fuels presently do not appear to be comparable with the conventional fuels in terms of economic viability, the aggressive research efforts in this area are likely to reduce the gap rapidly. The reduced environmental burden that these fuels offer will further serve as a significant incentive towards reducing the costs involved.

6. Conclusion

The transportation sector consumes a substantial portion of fossil fuel resources, and contributes greatly to atmospheric pollution by releasing GHG's, which are also responsible for the biggest environmental concern today, viz. global warming. With rapid depletion of fossil fuel resources and rising levels of GHGs, it has become imperative that these are replaced by alternative fuels which are less hazardous to the environment and also have the same efficiency as that of the conventional fuels. There are several alternatives that can be used as transportation fuels in place of the conventional fuels being used today. In order to successfully compete with conventional fuels, these alternative fuels however need to be improved in terms of their properties, production efficiency, and end-use suitability. Optimistically speaking, the magnitude of research efforts being put in this area should soon make the fossil fuels a thing of the past at least in the transportation sector, and consequently ensure that the future generations get a clean and green environment. Remaining petroleum may then better serve as a raw material for medicines, and thus as a boon for mankind!

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